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TECHNOLOGICAL CONDITIONS OF MELTING PROCESS FOR LEAD-CONTAINING GLASSES

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Aspects of mathematical modeling of the process of melting of lead-containing glasses used for production of ceramic paints are discussed. Based on laboratory studies, the stages of physicochemical transformations in batch and glass melt are established. The industrial experiments made it possible to determine the optimum temperature conditions for production of acid-resistant glasses. This provides the means for justified calculation of gas consumption in glass melting.

One of the main criteria of improving the quality of overglaze ceramic paints consists in improving their chemical stability, primarily, their resistance to the destructive effect of acids, as well as preservation of luster in decorated articles, which is determined by aesthetic requirements. This can be accomplished by improving the quality of the low-melting glasses which are the components of such paints. These glasses contain lead oxide, which improves various properties of the product. However, it has a negative effect on the acid resistance of glasses and paints made on the basis of these glasses.

Acid resistance depends on glass composition, structure, and arrangement of lead cations inside the glass structural lattice.

Research has revealed that it is impossible to completely solve the problem of stabilizing the acid resistance of glass by varying only the chemical composition of the mixture. A determining factor in this case is the temperature/time regime of melting of lead-containing glasses. Such regime ensures the preservation of a prescribed lead content and formation of certain structural groups within the glass structure whose lead cations exhibit high chemical bond energy.

Melting of lead-containing glasses is performed in horizontal batch-type rotary furnaces. Crushed and mixed glass batch components are charged into the furnace whose temperature is about 1000°C. The process of glass heating and melting begins immediately after the charging.

The contemporary approach to the problem of producing low-melting glass is based on mathematical modeling methods which allow for a sufficiently accurate description of the actual processes occurring during batch heating and glass melting.

In the context of the concepts of system analysis based on splitting initial problems into subproblems with subsequent joining of their solutions, the model of the considered problem appears as a combination of the ideal displacement model for the gas phase and the ideal mixing model for the solid (liquid) phase. The mathematical model equations in this case are presented in the following form:

$$G_g C_g \frac{d\theta}{dL} = \xi_1 \alpha_1 F_s (\theta - T_1) + \xi_2 \alpha_2 F_l (\theta - T_2);$$

$$\xi_1 G_s C_s \frac{dT_1}{d\tau} + \xi_2 G_l C_l \frac{dT_2}{d\tau} + \sum_i^n \beta_i \lambda_i \frac{dG_l^m}{d\tau} = \xi_1 \alpha_1 F_s (\theta - T_1) + \xi_2 \alpha_2 F_l (\theta - T_2) + r_a \Delta H + Q_h;$$

$$\lambda_i \frac{dG_l^m}{d\tau} = \alpha_3 F_r (T_2 - T_3);$$

$$\xi_1 = \begin{cases} 1, \ \dfrac{dG_i}{d\tau} = 0 \\ 0, \ \dfrac{dG_i}{d\tau} > 0 \end{cases};$$

$$\xi_2 = \begin{cases} 0, \ \dfrac{dG_i}{d\tau} = 0 \\ 1, \ \dfrac{dG_i}{d\tau} > 0 \end{cases};$$

$$\beta_i = \begin{cases} 0, \ T_i < T_i^m \\ 1, \ T_i > T_i^m \end{cases},$$

where G_g is the gas consumption; C_g, C_s, and C_l is the heat capacity of the gas, the batch, and the melt; θ is the gas me-

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dium temperature in the furnace; L is the furnace length; ξ_1, ξ_2 are the coefficients indicating the existence of convective heat transfer to the solid or liquid phases; α_1, α_2, and α_3 are the convective heat transfer coefficients in the gas-solid, gas-liquid, and liquid-solid systems; T_1 and F_s are the temperature and the surface area of the solid phase; T_2 and F_l are the temperature and the surface area of the liquid phase; T_3 and F_m are the temperature and the surface area of the solid SiO_2 particle in the melt; G_s and G_l are the quantities of the solid and the liquid phases in the system; τ is time; β is a coefficient indicating the existence of the melting process; G_i^m is the quantity of the melting substance in the system; λ_i is the melting heat of the ith component in the system; r_a is the chemical reaction velocity; ΔH is the reaction thermal effect; Q_h is the heat loss to the ambient environment.

The boundary conditions are $T(L, \tau)|_{L=0} = T^{en}(\tau)$;
$\theta(L, \tau)|_{L=0} = \theta^{en}(\tau)$.

The initial conditions are $T(L, \tau)|_{\tau=0} = T_0(L)$;
$\theta(L, \tau)|_{\tau=0} = \theta_0(L)$,

where T^{en} and θ^{en} are the temperatures of the glass melt and the gas flow entering the furnace; T_0 and θ_0 are the temperatures of the glass melt and the gas flow at the initial time moment.

Separate calculations for different states of aggregation, as well as taking account of heat released in melting of the batch components, are carried out by introducing the coefficients ξ_1, ξ_2, β_i which take discrete values [0, 1].

However, the model in this variant does not take into account the kinetic specifics of the process and does not specify which structural and chemical transformations take place in the batch and the glass melt under a particular technological regime, which is extremely important for comprehending the process and constructing a mathematical model which would relate the dynamics of the lead cation incorporation into the glass structural lattice to the temperature-time conditions for manufacturing acid-resistant glass. Therefore, it was necessary to conduct a series of experiments to obtain these dependences. The experimental research program contemplated the following:

qualitative analysis of the processes which occur in industrial glass melting;

X-ray phase analysis of the previous stage results;

determination of the effect of the batch heating dynamics on acid resistance of glass;

study of the variations in the chemical composition of glass melt in the course of industrial glass melting;

microscope analysis of acid-resistant and acid-nonresistant crystallized glasses to establish the type of crystal syngony;

X-ray phase analysis of crystallized glasses;

Glass of the $Na_2O - B_2O - PbO - SiO_2$ systems with Al_2O_3, ZnO, and TiO_2 additives was synthesized using industrial materials (red lead, borax pentahydrate, quartz sand, zinc white, alumina, and titanium oxide). The variations in the state of aggregation, weight, and color of the batch were consecutively analyzed for each 100°C starting with 100°C, after 30 min holding at each reference temperature. This experimental series was conducted up to the temperature of 1350°C which is the limiting temperature for the production technology. The gas medium inside the furnace was kept oxidizing to prevent lead reduction in glass melting.

At the temperature of 100°C, a certain weight loss was registered which continued up to the temperature of 500°C. The color of the batch changed within the temperature interval of 300 – 500°C. At the same time, a change in the batch volume and apperance of a strong sinter was observed, and at the temperature of 700°C the entire surface of the sinter was fused while its shape was preserved. An increase in temperature above 700°C resulted in complete spreading of the melt, which formed a smooth surface and still contained the gaseous phase and undissolved batch particles, and after holding at the final temperature (1350°C) a fluid transparent liquid emerged.

The qualitative changes observed in the course of the experiment were caused by the physical and chemical transformations occurring inside the initial batch in the glass melting process. The weight loss is caused by the removal of chemically bound water in the dehydration of borax. The change in the color of the batch powder is related to the redox processes and the chemical reactions occurring in the lead [1].

The process of phase formation at low heating temperatures was investigated. When the batch is introduced to the furnace at a temperature above 100°C, the borax melts and decomposes with formation of the compound $Na_2O \cdot 2B_2O_3$. Assuming that the most fusible eutectic is formed in the $PbO - B_2O_3 - SiO_2$ system (its melting point is 484°C), on further heating (temperature above 100 – 200°C) $Na_2O \cdot 2B_2O_5$ ought to interact with Pb_3O_4 and SiO_2 and form the compounds $5PbO \cdot B_2O_3 \cdot SiO_2$, $PbO \cdot SiO_2$, and $5PbO \cdot 4B_2O_3$ [2]. The lead oxide contained in the batch in this case should be totally spent on the formation of the above compounds.

An increase in temperature results in the formation of compounds in the $Na_2O - B_2O_3 - SiO_2$ eutectic system due to the existence of Na_2O and B_2O_3 which are not completely converted. The compounds which can be formed in this way are $Na_2O \cdot B_2O_3$ and $Na_2O \cdot 2SiO_2$ [2]. The remaining Na_2O with excessive SiO probably form the compound $Na_2O \cdot 2SiO_2$ [3].

The particular scheme of compound formation at a temperature prior to the start of melting is conjectural and takes into account the sequence of compound formation with increasing temperature of the eutectics.

X-ray phase analysis at low batch heating temperatures (up to 400°C) only showed the formation of lead silicates with different lead oxide contents. The microscope study confirmed the presence of these compounds as traces since their formation in the solid phase apparently requires protracted heating at low temperatures.

Taking into account all glass-forming components, one can expect the formation of more complex eutectic compounds in the $Na_2O - B_2O_3 - PbO - SiO_2$ system which convert to the vitreous state at the temperature of 500°C with complete dissolution of lead, sodium, and boron oxides in the glass. The x-ray analysis for this temperature only identified silica, and the microscope study revealed in addition, ZnO, Al_2O_3, and TiO_2 particles which are not yet dissolved in the melt. The x-ray pattern at the temperature of 500°C when a consolidated sinter with noticeably altered color is formed shows a reflection corresponding to β-SiO_2. This is due to the fact that at temperatures close to 500°C the eutectic melt in the $Na_2O - B_2O_3 - PbO - SiO_2$ system is formed virtually without any intermediate compounds.

An increase in temperature causes intense dissolution of SiO_2, and zinc, aluminum, and titanium oxides dissolve in the melt at temperatures between 900 and 1000°C, which is established by the microscope study. A further increase in temperature results in decreased viscosity and increased homogenization of the melt.

According to the conclusions derived from the experiment and taking into account the high rate of batch heating in industrial furnaces and the absence of protracted holding, it can be assumed that the formation of a eutectic melt in the $Na_2O - B_2O_3 - PbO - SiO_2$ system in the glass-melting furnace proceeds virtually without the formation of intermediate compounds.

The longevity of a paint coating is ensured by the conditions of the glass melting process. The presence of agitation contributes to disappearance of microinhomogeneities in the distribution of PbO and B_2O_3 in the melt. Maintaining the maximum glass-melting temperature, which should not lead to intense volatilization of PbO, makes it possible to obtain a melt without gas phase inclusions and undissolved particles. The batch heating rate in industrial furnaces should ensure the formation of the strongest bonds of Pb^{2+} cations in the glass structural lattice, which is accomplished by incorporation of Pb^{2+} cations into vacancies of the glass structural lattice and results in glass compaction [4].

An experiment in batch heating dynamics was carried out in industrial conditions (furnace diameter 1400 mm, furnace length 3200 mm). The experimental data are presented in Fig. 1. The main variable parameters were gas consumption, the ratio between gas and air consumption, and the furnace rotational speed.

A high degree of acid resistance in glass is accomplished by keeping the controlling parameters at a certain level to ensure the batch heating dynamics in accordance with curve *3* (Fig. 1). In such conditions the content of the lead cations identified in the acetic-acid extract does not exceed 1.7 mg/dm^2, which satisfies internationally accepted standards. A deviation of the temperature conditions from the optimum curve reduces the acid resistance and reduces the luster of paints based on these glasses.

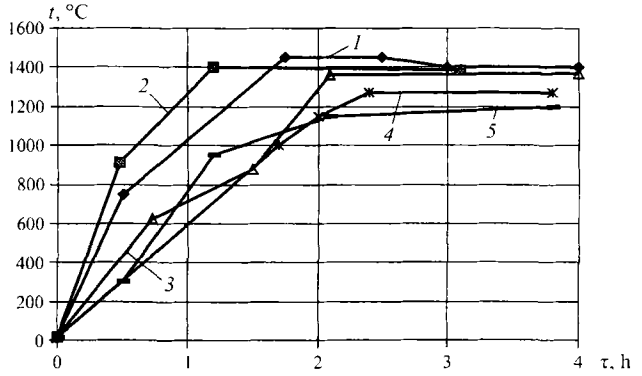

Fig. 1. Variation of temperature versus the duration of the batch and melt heating in glass melting: *1*, *2*) accelerated heating rate of batch and melt (*1* — exceeding the prescribed melting temperature); *3*) rational thermal conditions ensuring high acid resistance of glass; *4*, *5*) melting temperature below the prescribed temperature) (*4* — delayed stirring of melt during heating and melting; *5* — absence of stirring).

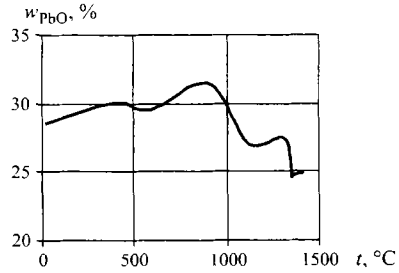

Fig. 2. Dependence of PbO content in glass on the melting temperature.

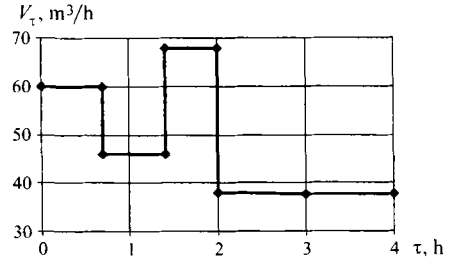

Fig. 3. Dynamics of rational gas consumption under the optimum glass-melting regime.

For a deeper understanding of the glass-melting process it is expedient to investigate the chemical composition of glass melt depending on the technological parameters (furnace length, temperature and duration of melting).

It is established that the chemical composition of the melt varies significantly depending on various factors. This is especially true for the lead oxide content which always tends to diffuse toward the melt surface and thus decreases the surface tension and, accordingly, the surface energy

[5, 6]. The mass content of lead oxide in samples varies at different periods of melting from 30 to 35%, which can produce increased volatilization. The content of Na_2O and B_2O_3 in samples varies to a lesser extent: from 2.5 to 4% and from 8 to 10%, respectively.

The variations of the main elements in the glass composition suggest that increased intensity of glass melt stirring is an essential factor of the glass melting process, since it improves the homogeneity of the entire melt body.

An attempt was made to evaluate the crystallizing properties of the acid-resistant and acid-nonresistant glass in order to elucidate their structural differences which eventually determine the glass quality. Samples of crushed glasses were heat-treated for the purpose of their crystallization.

The microscope analysis of such glasses made it possible to determine the extent of their crystallization and the difference in the crystalline phases they contained. The process of crystallization in the acid-resistant glass had been completed, as distinct from the acid-nonresistant glass whose degree of crystallization was approximately 50%.

Two phases are distinguished in crystallization of acid-resistant glass: one is in cubic syngony (its content is higher) and the other in non-cubic (monoclinal) syngony (its content is lower). In crystallization of acid-nonresistant glass only one phase in the tetragonal modification is revealed. The presence of a different crystalline structure point to a possible difference in the position of lead and boron (which are the most important elements determining the prescribed glass properties) in the glass structural lattice.

The x-ray phase analysis data substantiate the different variants of crystallization in two types of glass. Lead silicates of different modifications are presumably crystallized in the acid-resistant glass, whereas lead boron-silicates are crystallized in the acid-nonresistant glass.

Based on laboratory and industrial experiments, the optimum temperature regime of batch heating and glass melting that provides the required acid resistance and luster in the resulting glass was determined (Fig. 1, curve *3*). The process of incorporation of lead cations in the glass structural lattice in this case is implemented in such a way that all parameters of the process are efficient at each point of the curve (Fig. 2). The natural gas consumption needed to correspond to the constructed temperature curve was calculated using the described mathematical model (Fig. 3)

The performed investigations point to the complexity of producing lead-containing glass and the strong dependence of the process on numerous factors determining the optimum properties of glass. The combination of mathematical modeling with experimental investigations of all integrated glass-melting processes makes it possible to determine the optimum production technology parameters to produce glass of required quality.

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